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PATENTS ACT 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Magnesium-Zirconium Master Alloys and their Manufacture"

The invention is described in the following statement:

Magnesium-Zirconium Master Alloys and their Manufacture

Background and Prior Art

This invention concerns the addition of zirconium to pure magnesium or magnesium alloys and the preparation of magnesium-zirconium (Mg-Zr) master alloys.

Zirconium is a potent grain refiner for magnesium alloys that contain negligible Al, Mn, Si, Fe, Ni, Co, Sn and Sb (zirconium forms stable compounds with these elements) [1]. When added to these magnesium alloys in a proper quantity (normally around 1%), zirconium can readily cause the grain size to decrease by 80% or more under normal cooling rates. In addition, the unfavourable iron content can be readily brought down to under 0.005% from a normal level of 0.02-0.04% [2]. The exceptional grain refining ability makes zirconium an important alloying element for magnesium alloys that are not based on alloying with Al and Si. For example, zirconium containing Mg-RE-Zn alloys such as EZ33 (Mg-3.3RE-2.7Zn-0.6Zr) and ZE41 (Mg-1.2RE-4.2Zn-0.7Zr) offer a specific combination of elevated temperature and room temperature properties not achievable with the Mg-Al-Zn alloys [3].

The solubility of Zr in molten pure Mg is approximately 0.6% [3], which slightly increases with increasing melt temperature. The most characteristic feature of the microstructure of a magnesium alloy that contains more than a few tenths per cent soluble zirconium is the zirconium-rich cores that exist in most of the magnesium grains [4]. These zirconium-rich cores are believed to be the products of peritectic solidification [4]. In order to achieve excellent grain refinement in commercial production, it is desirable to dissolve the full zirconium content (i.e. 0.6%) in a magnesium melt [4].

To date, various approaches have been explored to introduce zirconium into molten magnesium. These include [1, 6]:

(a) alloying with different forms of zirconium metal,

(b) alloying with zirconium sponge,

(c) alloying with Zn-Zr master alloys,

(d) alloying with ZrO_2,

(e) alloying with various zirconium halides or complex halides or a mixture of halides and/or complex halides with different salts such as NaCl, KCl, $BaCl_2$, NaF, KF, etc, and

(f) alloying with Mg-Zr master alloys.

The advantages and disadvantages of each of these processes have been discussed in detail by Saunders and Strieter [6] and Emley [1]. For commercial manufacture, there have been only two types of zirconium alloying materials in widespread use since 1960 [1]. These are zirconium-rich Mg-Zr master alloys based on the fluoride and chloride salt reduction processes. Both types of master alloy are essentially the same and contain about one third their weight of zirconium [1]. One of them, developed by Magnesium Elektron Ltd. (MEL) via chemical reduction of zirconium fluoride with molten magnesium, has been long known as Zirmax (trade mark). This development was first made by MEL as far back as 1945 [1]. The similar type of Mg-Zr master alloy developed in the United States approximately during the same period was based on a chloride salt reduction process [6]. But it was not until about 1960 that MEL replaced its salt reduction alloying processes by Zirmax. Before that (from 1947 to 1959) master salt was used for virtually all magnesium-zirconium alloy production in the UK and other European countries, and to a gradually increasing extent in the USA [1].

At present the Zirmax type master alloy is still the primary zirconium alloying material used for the commercial production of zirconium-containing magnesium alloys. It contains approximately 33% Zr and 67% Mg and most of the zirconium is present as various sizes of zirconium particles (mostly in the range of submicron to 10μm) in a magnesium matrix [7].

Sauerwald [8] published his work on alloying zirconium metal powder to magnesium in 1947. He added 5wt% zirconium metal powder to magnesium under an argon atmosphere at various temperatures between 680 and 1100°C. Soluble zirconium contents exceeding 0.5 wt% (samples were digested in HCl acids) were obtained at all temperatures tested. Ball [9] in the same year described the British work and stated that metallic zirconium dissolves in magnesium under an argon atmosphere at 900-1100°C but it is a difficult and costly process. Emley [10] in 1948 pointed out that as the zirconium metal powder is expensive and highly inflammable, it is natural to consider the possibility of alloying by a reducible zirconium compound.

In 1952, Saunders and Strieter [6] published their work "Alloying Zirconium to Magnesium", in which different metallic forms of zirconium, i.e zirconium sponge, fused zirconium, iodide-decomposed ductile zirconium, and zirconium powder, were investigated as zirconium alloying materials for magnesium at 760°C (1400°F). The fused lump zirconium was added as 6.35-mm (¼-in.) pieces in a small steel ladle and stirred in the ladle with a steel rod. No apparent solution had occurred after 30 minutes of stirring. Analysis of the melt showed a result of 0.03% soluble zirconium content with 1% zirconium addition. Iodide zirconium sheet, rolled to about 127–254μm (0.005-0.010 in.) and cut into 6.35-mm (¼-in.) squares was added in a manner similar to that used for the fused lump zirconium. It was stirred for several minutes in the ladle. It was found that after 65 minutes of holding at temperature, the resultant soluble zirconium content merely reached 0.1% with 1% zirconium addition. The use of zirconium powder was evaluated by adding it in different ways. This is because zirconium powder is pyrophoric and some means of protecting the powder from oxidation had to be applied. In the work referenced [6], materials tested were zirconium powder pelleted with various binders, zirconium powder enclosed in tight magnesium capsules, sintered zirconium powder briquettes, and zirconium powder compacted with magnesium powder. In general, with 3% zirconium addition to a Mg-5Zn melt, the resultant zirconium content varied between 0.7 and 0.85% as reported.

The solubility of zirconium in magnesium is influenced by the presence of a third element. It is reported that with the presence of Zn at a level around 3-4%, the solubility of Zr in magnesium could be increased from 0.6% to slightly over 0.7%, and with 5% zinc in the magnesium the solubility of Zr increases to about 0.8% [6].

According to Saunders and Strieter [6], of the various metallic forms of zirconium tested, alloying with zirconium sponge demonstrated the most promising results. The zirconium sponge used was made by the Kroll process (sublimation of Mg and Mg_2Cl from the reaction product of Mg + $ZrCl_4$) [6]. In their experiments, the sponge was essentially ground with the average size being reduced to about 12.7 μm or 0.0005 in. The results showed that zirconium sponge produced a soluble zirconium content of about 0.62-0.66% in Mg-5Zn alloys with 3% zirconium addition after 3-4 minutes stirring. With 1% zirconium sponge addition, soluble zirconium contents in the range of 0.32 to 0.52% were achieved. Furthermore, the authors found that the alloying efficiency decreased when the sponge fragments were decreased in size because when the particles became finer powder, the material burned up before it could be submerged beneath the melt. Therefore, some means of protecting the powder from oxidation had to be applied.

Despite the excellent alloying results demonstrated by the work of Saunders and Strieter [6] with Kroll process zirconium sponge, alloying zirconium sponge to magnesium was in general limited to laboratory scales. As realised and pointed out by Saunders and Strieter [6], "an important disadvantage in the commercial use of sponge in the magnesium alloying field is the rather laborious effort required to alloy the material". This laborious effort apparently refers to the grinding process because the alloying process employed, i.e. 3-4 minutes of stirring, was plainly simple. In addition, the unavoidable contamination problem arising from the grinding process is another important disadvantage to such commercial use of zirconium sponge.

The remarks given by Emley [1] in his well-known *Principles of Magnesium Technology* about alloying zirconium metal to magnesium are: "pure zirconium metal

is expensive by any route and very inflammable in powder form, and for these reasons, coupled with the ease with which it becomes contaminated with oxygen, hydrogen and nitrogen, the approach via zirconium metal is not obviously the best".

Experiments have indicated that in commercial production of magnesium alloys, when Zirmax is dissolved into a magnesium melt at commercially useful addition rates, undissolved zirconium particles can be readily observed in the microstructure of the magnesium alloy produced [7, 11]. Many of these residual (undissolved) zirconium particles have an average size of around 5μm. It would be desirable if these zirconium particles could be smaller than those produced by using Zirmax so that more zirconium particles were available for nucleation of magnesium grains. Much improved grain refinement could be achieved by a denser nucleation.

The density of zirconium is $6.5 gcm^{-3}$ whereas that of molten magnesium is $1.6 gcm^{-3}$. Therefore zirconium particles have a strong tendency to settle in the melt unless stirred vigorously [7]. The larger the particle, the faster it settles out to the bottom of the melt. For example, a 15 micron zirconium particle falls at approximately 40 mm/min to the bottom of a magnesium melt at 780°C and is therefore difficult for these particles to maintain suspended in the magnesium melt at this temperature [7]. By contrast, when the particle size is smaller than 3 microns, it can be readily suspended in the magnesium melt at the same temperature [7].

References for the above discussion are:

[1] E. F. Emley, Principles of Magnesium Technology, Pergamon Press, Oxford, 1966, pp. 127-155.

[2] Ref. [1], p. 184.

[3] A. Luo and M. O. Pekguleryuz, "Review: Cast magnesium alloys for elevated temperature applications," J. Mater. Sci., 1994, Vol. 29, pp. 5259-71.

[3] A. A. Nayeb-Hashemi and J. B. Clark, Phase Diagrams of Binary Magnesium Alloys, ASM Metals Park, Ohio, 1988, pp. 365-369.

[4] Ref. [1], pp. 257-261.

[6] W. P. Saunders and F. P. Strieter, "Alloying zirconium to magnesium", Transactions of the American Foundrymen's Society, 1952, Vol. 60, pp. 581-594.

[7] Ma Qian, L. Zheng, D. Graham, D. H. StJohn and M. T. Frost, "Settling of undissolved zirconium particles in pure magnesium melts", Journal of Light Metals, 2001, Vol. 1, No.3, pp. 157-165.

[8] V. F. Sauerwald, "Dus Zustandsdiagram Magnesium-Zirkonnium", Zeitschrift fur anorganische Chemie., 1947, Band 255, pp. 212-220.

[9] C. J. P. Ball, Metallurgia, 1947, Vol. 35, pp. 125-129; 211.

[10] E. F. Emley, Discussions of the Faraday Society, 1948-49, Vol. 47, No. 4, pp.219.

[11] Y. Tamura, N. Kono, T. Motegi and E. Sato, "Grain refining mechanism and casting structure of Mg-Zr alloys", Journal of Japan Institute of Light Metals, 1998, Vol. 48, No. 4, pp. 185-189.

Summary of the Invention

An aim of the present invention is to provide a different route for the preparation of a Mg-Zr master alloy which may contain up to 50 wt% zirconium or more. It is expected that the process will produce a master alloy much more cheaply than existing processes.

Another aim is to provide a Mg-Zr master alloy where the larger zirconium particles present in the master alloy are much smaller than those in presently available master alloys. Owing to the presence of the smaller zirconium particles provided by the invention, superior grain refinement can be readily achieved using this new master alloy.

Accordingly, in one aspect the invention provides a method of manufacturing a master alloy of zirconium in magnesium, said method comprising:

(i) selecting a metallic sponge containing zirconium,

(ii) washing the sponge in an acid solution,

(iii) submerging the washed sponge in molten magnesium and stirring the molten metal to create a suspension of fine zirconium particles in molten magnesium, and

(iii) casting the magnesium-zirconium melt into ingots.

The master alloy may comprise 10%-50% zirconium in magnesium, more preferably in the range 20% to 40% zirconium in magnesium.

Preferably the master alloy has zirconium particles sized 90% less than 3 μm and average size less than 5 μm.

The sponge may be rinsed and dried after the washing step. The sponge is preferably a porous agglomerate of metallic grains.

The acid solution may be HF at a concentration between 0.10% and 50.0%, preferably between 0.50% and 5.0% and more preferably between 1.5% and 2.5%, with the acid concentrations calculated as shown elsewhere in this specification. These acid concentration ranges correspond respectively to 0.05 – 50.0 molar, 0.25 – 2.63 molar and 0.76 – 1.28 molar, which may be rounded to 0.05 – 50, 0.25 – 3.0 and 0.75 – 1.5 molar.

Preferably the sponge comprises zirconium with only incidental impurities. Hafnium is a common impurity in zirconium. In contrast, Fe, Ni, Mn, Al, Si, C, Co, Sn and Sb are undesirable as they are alloying inhibiting and their total concentration is preferably less than 1% and more preferably less than 0.5%.

Preferably the zirconium sponge is in the physical form of small particles and each particle has a porous structure. Preferably these zirconium sponge particles have the following properties:

- the particles have an average size between 0.1 to 10 mm, more preferably between 0.5 and 5mm

- the particles have a minimum size of 0.5mm, more preferably 1mm, and a maximum size of 10mm, more preferably 5mm
- density of sponge = 5.2-6.3g/cm^3, more preferably 5.5-5.8g/cm^3
- porosity of sponge (1 – (density of sponge)÷(density of solid zirconium)) 0.08-0.2, more preferably 0.11-0.15
- the void sizes on a polished transverse section of each zirconium sponge particle are in general between 5 and 60 μm.

In a further aspect the invention may provide a method of adding an alloying element to a molten metal, comprising:

(i) selecting a metallic sponge containing the alloying element,

(ii) washing the sponge in a source of fluoride ions, and

(iii) submerging the sponge in said molten metal and stirring the molten metal.

In another aspect the invention provides a method of manufacturing a master alloy of zirconium in magnesium, said method comprising:

(iv) selecting a metallic sponge containing zirconium,

(v) washing the sponge in a source of fluoride ions,

(vi) submerging the washed sponge in molten magnesium and stirring the molten metal to create a suspension of fine zirconium particles in molten magnesium, and

(iv) casting the magnesium-zirconium melt to solidify as said master alloy.

Preferably said master alloy is cast as ingots, which term is intended in this specification to include briquettes, pellets and the like.

The sponge may be rinsed and dried after the washing step. The sponge is preferably a porous agglomerate of metallic grains.

The source of fluoride ions may be an acidified solution containing fluoride ions or may be hydrofluoric acid at a concentration between 0.10% and 50%, preferably

between 0.50% and 5.0% and more preferably between 1.5% and 2.5% when calculated as described elsewhere in this specification.

Brief Description of the Figures

In order that the invention may be more fully understood there will now be described, by way of example only, preferred embodiments and other elements of the invention with reference to the accompanying illustrations where:

Figure 1 is a photograph showing the physical form of zirconium sponge particles as used in one embodiment of the present invention.

Figure 2 is a micrograph showing a view of a typical microstructure of the zirconium sponge particles shown in Figure 1.

Figure 3 is a micrograph showing a view of an alternative microstructure for the zirconium sponge particles shown in Figure 1.

Figure 4 is a schematic diagram illustrating the method of adding zirconium sponge to molten magnesium.

Figures 5 and 6 show typical views of the microstructure of an ingot produced according to the present invention.

Figures 7 and 8 show typical views of commercially available Zirmax master alloy.

Description of Examples of the Invention and the Preferred Embodiment

The procedures followed are set out in the following steps numbered 1 to 6.

1. Comparison Trials

A zirconium sponge in the physical form of zirconium sponge particles of size 1-10 mm diameter was selected. The major impurity in the sponge was hafnium. The impurity concentrations were:

Hf = 0.8% approx

Fe+Cr = 0.1%

C = 0.004%

H = 0.001%

N = 0.002%

The sponge was added, without pretreatment, to two samples of molten magnesium at 730 and 780 °C respectively. Cone samples (ϕ30×ϕ20×25 mm) were collected at different times and examination showed little evidence of grain refinement even when the melt was held at 780 °C for 2 to 6 hours. Wet chemical analyses of the soluble zirconium contents in the samples using 15% HCl acid showed negligible zirconium contents (< 0.05%).

2. Washing and cleaning stage

Zirconium sponge identical to that used in the comparison trials above was first washed in an acid solution which was prepared in the following manner:

> 45ml concentrated nitric acid (68.5%-69.5%) and 45ml concentrated hydrofluoric acid (50%) were combined and diluted in water to a total of 1000ml. This gave an acid solution of approximately 3% HNO_3 and 2% HF, which equates to approximately 1.1 molar HF and 0.5 molar HNO_3.

The zirconium sponge was left in this acid solution for 5 minutes. Bubbling was observed which indicated that the acid had probably at least partially removed the ZrO_2 layer and was dissolving some of the zirconium metal underneath. The zirconium sponge was then rinsed in ethanol and dried.

An alternative washing process which was found satisfactory comprises washing the sponge in 0.25-0.5% HF. This is a very dilute HF acid solution and is readily handled. 0.5% HF was prepared by diluting 1ml concentrated Hydrofluoric acid (50%) to 100ml with water.

Concentrated nitric acid does not seem to work. Aqua regia works very slowly. The use of a heating plate slightly improves the washing process.

Although it is thought that successful washing involves the dissolution or some physical removal of oxide from the Zr surface, we do not wish to be bound by any theory as to why such a washing step is effective.

3. Drying stage

The washed and rinsed zirconium sponge was dried under heating lamps at approximately 50°C for 60 minutes.

4. Addition stage

A hole was machined into a small piece of magnesium ingot and the required pieces of zirconium sponge were placed into the hole as illustrated in Figure 4. This piece of ingot was then quickly submerged below the magnesium melt surface. This allowed the zirconium sponge to be introduced directly to the melt without the possibility of it remaining on the surface of the melt. It avoided oxidation of the Zr, avoided it being trapped into dross, and avoided the Zr not being wetted by the melt. The sponge could be added to the melt in other ways, such as by adding a compact of sponge particles, providing that it is successfully introduced below the surface.

It has been found that, alternatively, the zirconium sponge particles can be directly added to the melt under certain circumstances. An example is if the magnesium melt

surface is protected with cover gas such as 1% SF_6 (balance: 49.5% CO_2 and 49.5% dry air) and the concentration of oxygen above the surface of the magnesium melt is therefore very low, the sponge particles can be successfully added directly providing it is done quickly. For example, the zirconium sponge particles can be added at a height of 800 mm away from the melt surface through a steel funnel, where the bottom of the funnel is placed just above the melt surface. This allows the sponge particles to quickly get into the melt without being oxidised. This has been proved to be a very convenient way of adding small (< 5mm) zirconium sponge particles to magnesium melts.

5. Alloying stage

A total of 180g zirconium sponge particles were added to a 550g magnesium melt at 730°C. The nominal addition of zirconium was approximately 25 wt%. These zirconium particles were added in six batches, i.e., 15, 20, 20, 25, 35 and 35 g. Gentle manual stirring was applied throughout the whole alloying process (60 minutes).

Cone samples were collected after addition of each batch of zirconium sponge particles. Figures 2 and 3 show typical views of the microstructure of the zirconium sponge. Owing to the gradual dissolution of the porous structure, each zirconium sponge particle will eventually be disintegrated into many fine zirconium particles sized around 2 to 3μm. It is important to keep gentle stirring throughout in order to produce a suspension of fine zirconium particles in the melt.

6. Casting stage

The magnesium-zirconium melt produced as described above can be cast into different moulds, preferably into chill moulds. Preferably the mould employed has an excellent chilling effect. Where possible, a low casting temperature such as 680 °C or lower is preferred. Cover gas should be used during casting.

Figures 5 and 6 show typical views of the microstructure of an ingot produced according to the above description with 20% zirconium addition. The white phases are zirconium particles. Figures 7 and 8 show typical views of MEL's Zirmax master alloy. As can be seen, the zirconium particles present in the alloy of the present invention are in general smaller than those present in Zirmax. Small zirconium particles are always highly preferred as discussed earlier.

Three preliminary tests conducted at 680, 730 and 800 °C have shown that the use of the present invention can readily achieve soluble zirconium contents close to or even greater than 0.50% after 30 minutes of alloying process. By contrast, the use of Zirmax usually results in soluble zirconium contents typically around 0.40% under the same experimental conditions.

6. Further Discussion

XPS analyses of treated and untreated sponge particles gave the results shown in the following table. For each analysis given, information was collected from a depth of 5 nanometers or 10 atomic layers on the surfaces of six different large particles.

Sponge Particles	Surface composition in atom percentage								
	C	O	Zr	Fe	Si	F	Cl	Mg	Hf
Untreated	30.5	49.2	16.2	1.1	3.0	0	0	0	0
Treated particles (black)	10.3	43.3	14.9	1.3	2.3	27.8	0	0	0
Treated particles (grey)	26.0	41.1	15.6	1.1	1.7	27.4	0	0	0

According to the energy level detected for each element, it is confirmed that O is present in the form of ZrO_2 in all three cases studied and the detected F in the treated particles is present in the form of ZrF_4 in all three cases studied.

The extra O (Zr:O = 1: 2 in ZrO_2) is most likely due to the presence of oxidised C, Fe and Si on the surface.

For both treated and untreated particles, the surface is covered with a layer of ZrO_2. The atom percentage of O does not change much after treatment.

Although we do not wish to be bound by any theory, it is presently thought that the mechanism is that there might be some defects or tiny voids existing on the surface or there are some "weak" sites on the ZrO_2 and that these sites are attacked by the dilute HF solution. Consequently, tiny patches of ZrF_4 would be formed on these attacked sites. Owing to the formation of such ZrF_4 patches, oxidation of zirconium would be prevented on these sites after treatment. It is thought that the ZrF_4 then dissolves into molten magnesium, leaving parts of the zirconium surface exposed to the molten magnesium even though most of it is still protected by a ZrO_2 covering. When such treated particles are introduced into molten magnesium, the dissolution of different patches or ZrF_4 on the particle surface would provide many fresh contact sites or channels with molten magnesium. This causes the dissolution of the whole sponge particle. Note that there are many tiny channels existing in each sponge particle as revealed by the BSE images. This would explain the disintegration of the sponge particles.

The above proposed mechanism is offered only as a possible explanation of the experimental results and there could be other mechanism(s). The present invention may incorporate but is not to be considered limited by the mechanism described.

Whilst the above description includes the preferred embodiments of the invention, it is to be understood that many variations, alterations, modifications and/or additions may be introduced into the constructions and arrangements of parts previously described without departing from the essential features or the spirit or ambit of the invention.

It will be also understood that where the word “comprise”, and variations such as “comprises” and “comprising”, are used in this specification, unless the context requires otherwise such use is intended to imply the inclusion of a stated feature or features but is not to be taken as excluding the presence of other feature or features.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that such prior art forms part of the common general knowledge in Australia.

Dated this 18th day of January 2002

CAST Centre Pty Ltd

by their patent attorneys Morcom Pernat

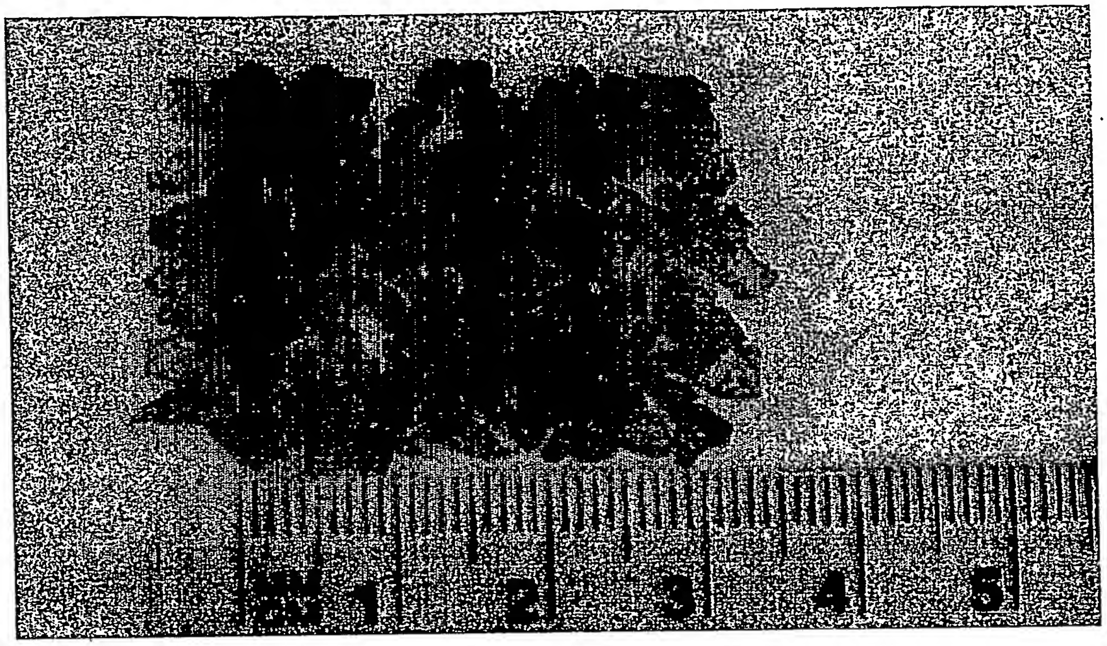


Fig. 1

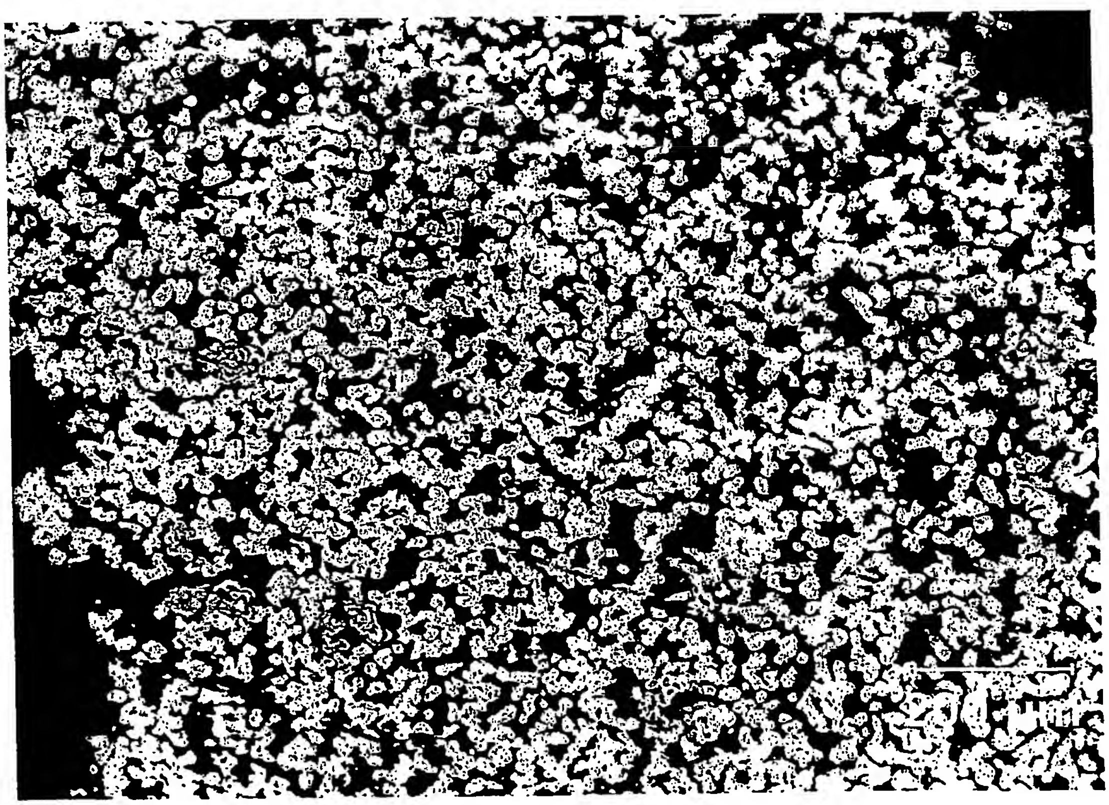


Fig. 2

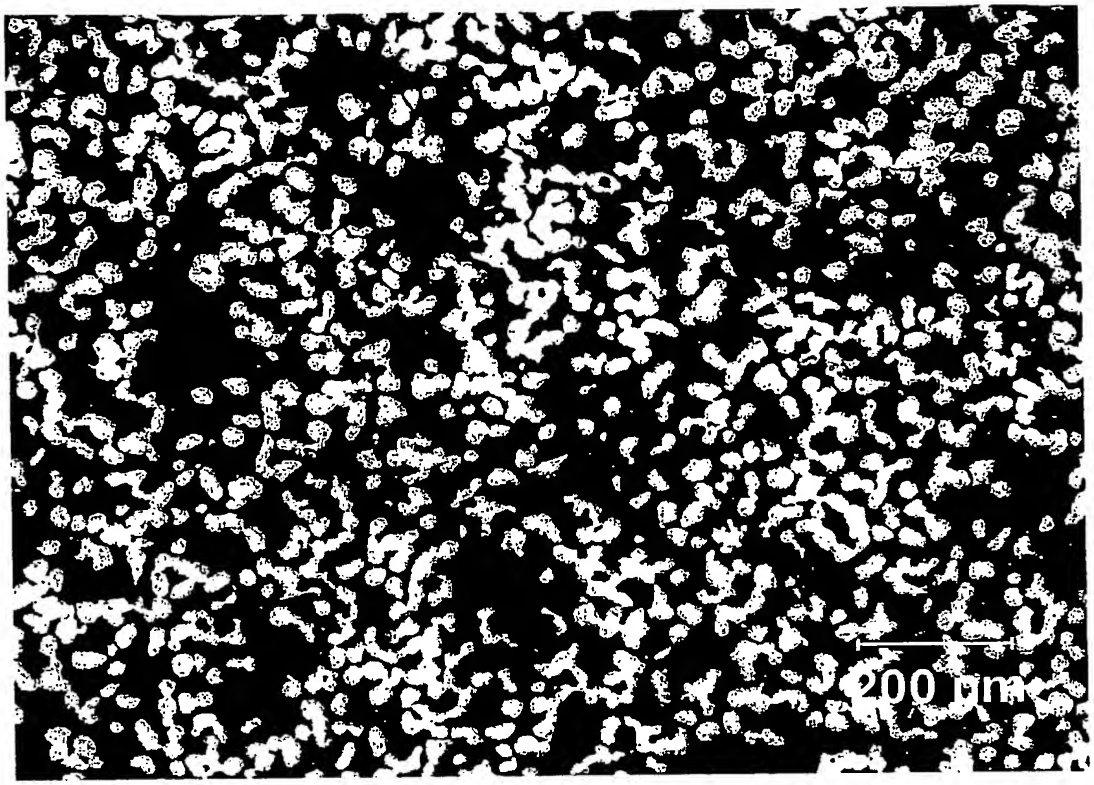


Fig. 3

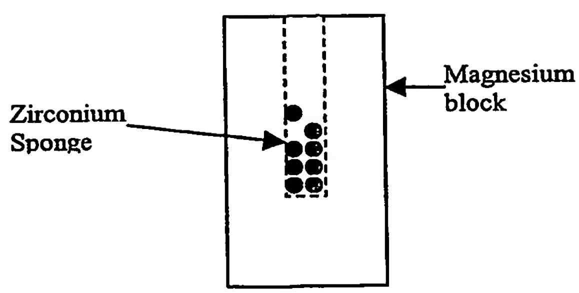
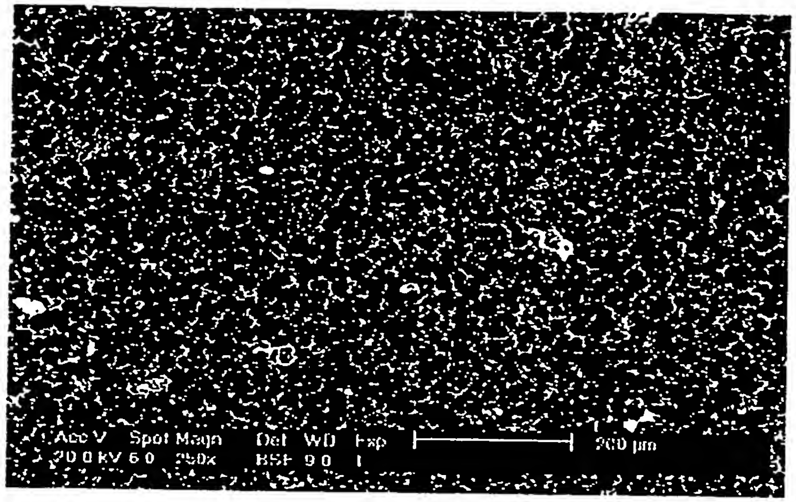


Fig. 4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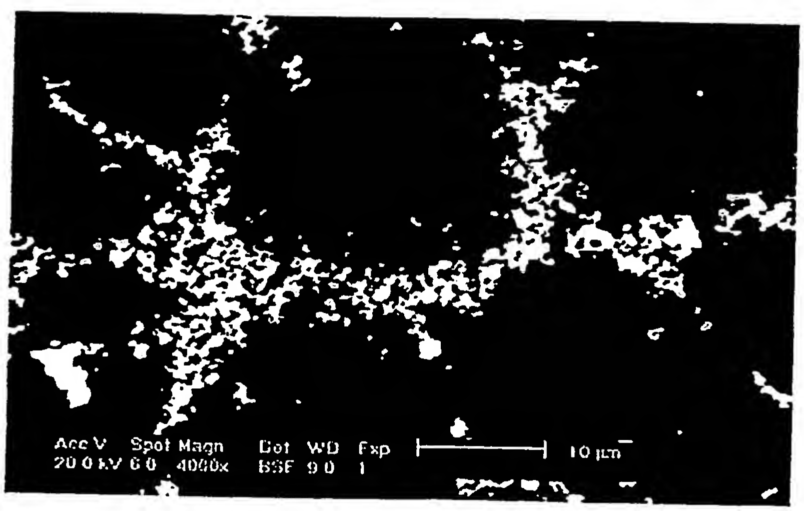
20.0 kV 6.0 250x BSE 9.0 1

Fig. 5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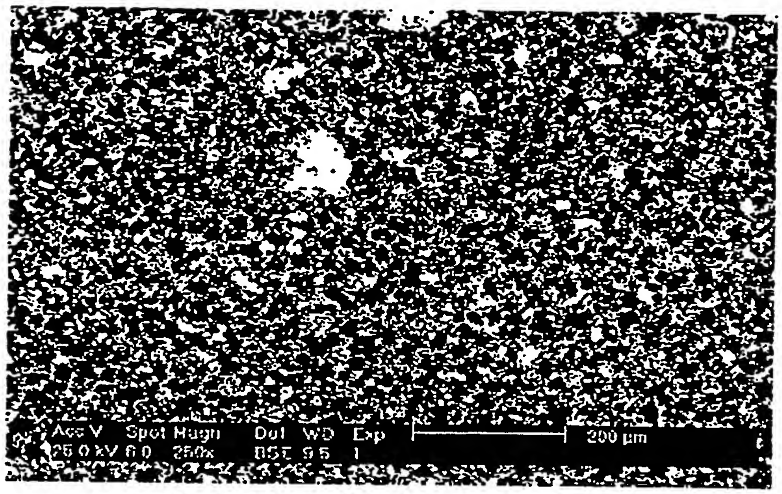
10 µm

Fig. 6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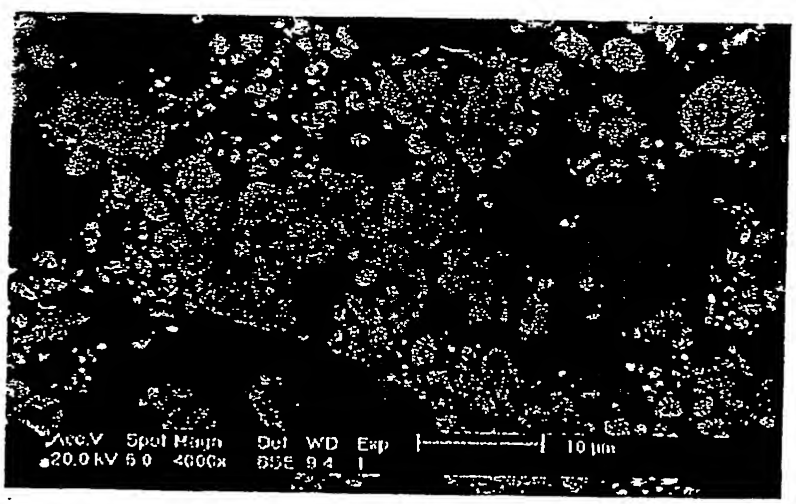
200 µm

Fig. 7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10 µm

Fig. 8